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# Reversible Addition of Cyanide to Triphenylamine Attached Difluoroboron $\beta$ -Diketonate Facilitated Selective Colorimetric and Fluorimetric Detection of Cyanide ion

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Dedication ((optional))

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**Abstract:** Nucleophilic addition of cyanide on a new triphenylamine attached difluoroboron  $\beta$ -diketonate (4-(4-(diphenylamino) phenyl)-2,2-difluoro-6-methyl-2H-1,3,2-dioxaborinin-1-ium-2-uide (C4)) breaks the conjugation readily and thereby offers efficient and selective detection of cyanide. A rational mechanism based on UV-Vis, fluorescence, NMR (<sup>1</sup>H, <sup>11</sup>B, and <sup>19</sup>F) and HRMS analysis and DFT calculations have been proposed. The detection limit was found to be 0.36  $\mu$ M. A test strip assay using the title compound has also been applied to detect CN<sup>-</sup> in aqueous solution for real-time applications.

#### Introduction

Development of small molecules for anion recognition has received considerable attention over the last 25 years due to their influential role in far-ranging biological, environmental, and chemical applications.<sup>[1]</sup> Among the several anions, cyanide ion (CN<sup>-</sup>) is a highly toxic inorganic anion, which is still extensively used in various industrial processes such as electroplating, gold mining, tanning, metallurgy, plastic manufacturing and production of synthetic fibers and resins.<sup>[2]</sup> It is also found in agricultural products such as cassava roots and bamboo shoots.<sup>[3]</sup> Cyanide ions are generated by hydrolysis of phosphate-based chemical warfare agents.<sup>[4]</sup> Throughout the world, consumption of cyanide is as much as 1.5 million tons per year.<sup>[5]</sup> Cyanide ion has a greater affinity to cytochrome c oxidase to forms a complex in the human bloodstream which results in respiratory arrest and finally leads to death when consumption exceeds 0.05 mg kg<sup>-1</sup> of body weight.<sup>[6]</sup> The maximum permissive level of cyanide ion in drinking water is specified as 1.9 µM (70 ppb) by the World Health Organization (WHO).<sup>[7]</sup> Thus efficient and selective detection of cyanide ion is a highly desirable task. Various conventional methods have been developed for quantitative detection of titrimetric.<sup>[8]</sup> electrochemical.<sup>[9]</sup> cvanide ion like spectrophotometric,<sup>[10]</sup> and chromatographic analyses.[11] However, these methods have different limitations such as large time consumption, high cost and requirement of highly skilled operators. In recent days, development of fluorescent probes as optical sensors for selective and sensitive detection of cyanide ion has been explored with cost-effectiveness and simple-to-use alternatives in focus.<sup>[12]</sup> These sensor systems have their advantages like operational simplicity, fast detection and feasibility for naked-eye detection which eventually creates an excellent tool for on-site analysis.<sup>[13]</sup> Different sensors have been reported so far based on hydrogen bonding interaction, supramolecular self-assembly, coordination of cyanide ion with a metal ion, boronic acid derivatives, nucleophilic addition reaction, deprotonation, etc.<sup>[14]</sup> Among these, particular interest has been devoted to designing fluorescent probes based on oxazine, pyrylium, indolium, pyridinium, acridinium, imidazole, dicyanocarbazole, quinoline, salicylaldehyde, vinvl group, trifluoroacetamide derivatives, and other highly electron-deficient carbonyl compounds for selective detection of cyanide ion.<sup>[15]</sup>

Difluoroboron  $\beta$ -diketonate complexes have gained much attention in recent years due to their unique photophysical properties and have been shown to possess a wide range of applications.<sup>[16]</sup> In this manuscript, we present a triphenylamine attached difluoroboron  $\beta$ -diketonate based fluorescent sensor (**C4**) for highly selective and sensitive detection of cyanide ion over other anions. This simple probe has an interesting feature that nucleophilic addition on the carbonyl can disturb the conjugation and, consequently, the optical properties. This system is different from the conventional dicyanovinyl based Michael acceptors used for the sensing of cyanide ion.<sup>[150, 15r, 17]</sup> In the dicyanovinyl systems, the nucleophilic addition of cyanide ion takes place at the  $\beta$ -carbon and breaks the conjugation of the

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chromophore group with the cyano groups completely and hence no ICT is observed between them. In the system presented in this manuscript the nucleophilic addition of cyanide ion takes place at the 1,3- $\beta$ -ketonate carbon with the blue shift of ICT between the amine and the BF<sub>2</sub> groups. In addition, this system offers reversibility in the presence of excess water. Interaction of cyanide ion with **C4** is accompanied by the formation of an anomalous emission and color change from yellow to colorless via intramolecular charge transfer mechanism.

### **Results and Discussion**

**Synthesis and Characterization:** The synthetic route for the preparation of **C4** is simple and it was obtained in high yield by following the Scheme 1.<sup>[18]</sup> Incorporation of BF<sub>2</sub> was carried out by refluxing 1, 3-diketone substrate **3** with BF<sub>3</sub>·OEt<sub>2</sub> in dichloromethane. The structure of the compound **C4** was confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>11</sup>B and <sup>19</sup>F NMR, ATR-IR and HRMS spectra (Figure S7-S12).



Scheme 1. The synthetic route of C4.



Figure 1. Absorption and emission spectra of C4 in various solvents.

The absorption and emission spectra of **C4** in different solvents with varying polarity are shown in figure 1, and their corresponding photophysical data are gathered (Table ST1, Supporting Information). **C4** showed a strong and intense absorption band around 425 nm in all the solvents investigated which is ascribed to intramolecular charge transfer (ICT) from triphenylamine donor moiety to the difluoroboron acceptor moiety within the molecule. As the solvent polarity is increased within polar aprotic solvents from acetone to dimethyl sulfoxide a slight red shift was observed (423 to 432 nm) which indicates the stabilization of ICT transition. The emission spectra presented in figure 1b is also red shifted (530 to 567 nm) with increase in solvent polarity as similar to absorption spectra due to the stabilization of ICT process within the molecule.



Figure 2. Absorption and emission spectra of C4 (7  $\mu M)$  in the presence and absence of CN (0-400  $\mu M)$  in acetonitrile/water (98:2) solution.

# Absorption and emission spectral studies in the presence and absence of anions

The absorption and emission spectra of **C4** in the presence and absence of cyanide ions (tetrabutylammonium cyanide) in acetonitrile:H<sub>2</sub>O (98:2) are shown in figure 2. The acetonitrile:H<sub>2</sub>O (98:2) system was chosen for cyanide ion sensing based on the photophysical results obtained from a series of experiments with different fractions of water in acetonitrile.<sup>[18]</sup> Appreciable change in absorption and emission properties was noted in solvents systems containing less than 10% of water in acetonitrile. On

increasing the concentration of CN-, the intensity of ICT absorption band centered at 425 nm decreases along with the formation of a new absorption peak at 320 nm. The formation of an isosbestic point at 364 nm indicates the 1:1 interaction between the C4 and CN<sup>-</sup>. The stoichiometry between C4 and CN<sup>-</sup> was again confirmed from the Job's plot. As shown in the Job's plot curve (Figure S15, supporting information), the measured absorbance variation at 320 nm reached a maximum value when the molar ratio of [C4]/([C4] + [CN<sup>-</sup>]) was 0.50, which indicated an 1:1 interaction between C4 and CN<sup>-</sup>. At a higher concentration of CN<sup>-</sup>, the absorption band at 425 nm disappeared completely and the new band at 320 nm was only visible. This is due to the fact that electron density at acceptor moiety increases after the nucleophilic addition of CN<sup>-</sup> which results in the formation of a new ICT state leading to the complete disappearance of the old ICT band at 425 nm. This change in the ICT behavior resulted in a color change from yellow to colorless indicating that compound C4 could serve as a colorimetric probe to detect CN<sup>-</sup> with naked eye (Figure 2a). The fluorescence spectra of C4 in acetonitrile:H<sub>2</sub>O (98:2) were recorded by exciting at the isosbestic point (272 nm) after every addition of aliquots of tetrabutylammonium cyanide solution of known concentration to it. As shown in figure 2b, C4 is non-fluorescent at this excitation wavelength in the absence of CN<sup>-</sup>. In contrast, the presence of CN<sup>-</sup> led to the formation of a new emission peak centered at 402 nm. The gradual addition of cyanide ion led to fluorescence enhancement at 402 nm due to the formation of a new ICT state.



Figure 3. Absorption and emission spectra of C4 (7  $\mu M)$  with various anions (60  $\mu M)$  in acetonitrile/water (98:2) solution.

Selectivity and effect of anion interference

To evaluate the selectivity of cyanide ion over other anions, the optical response of C4 in 98% acetonitrile with various anions in excess were evaluated using absorption and emission spectral studies (Figure 3). Among the tested anions (CN<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>, AcO<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, HSO<sub>4</sub><sup>-</sup>, IO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>) as their tetrabutylammonium salts at 10 equivalents excess concentration (60 µmol), the probe responded only to the cyanide ion with a remarkable color change from yellow to colorless. The addition of fluoride ion in excess also caused a slight influence on the absorption spectrum of C4, but with much lower sensitivity than that of CN<sup>-</sup>. The absorption and emission spectra of C4 in the presence and absence of F- are depicted in figure S16 (Supporting Information). In contrast to the absorption spectrum, there is no change in the fluorescence spectrum in the presence of F<sup>-</sup>. It was the case with the other anions as well. F<sup>-</sup> is highly solvated in water and loses its basicity due to hydration in acetonitrile-water mixture. The slight change observed in the absorption spectrum may be due to the change in the solvation around the C4 molecule. The comparatively lower hydration energy for the cyanide ion ( $\Delta H_{\text{hyd}}$  = -64 kJ/mol) than that of the fluoride ion ( $\Delta H_{hvd}$  = -505 kJ/mol) may be the reason for the higher selectivity and sensitivity of C4 towards cyanide ion.[19]



**Figure 4.** Competitive experiments in the **C4**-CN<sup>-</sup> system with interfering anions ( $\lambda_{ex} = 272$  nm). Selectivity profiles of **C4** (7  $\mu$ M) in the presence of 60  $\mu$ M of various anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>, AcO<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, HSO<sub>4</sub><sup>-</sup>, IO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>) in acetonitrile/water (98:2) with or without CN<sup>-</sup>.

To further explore the utility of **C4** as an ion-selective fluorescent sensor for CN<sup>-</sup>, the effect of other anion interference on the detection of CN<sup>-</sup> was carried out upon the addition of 10 equivalents of other anions individually and all other anions combined in 98% acetonitrile solution (**Figure 4**). These results indicate that other anions did not induce any significant changes in the presence of CN<sup>-</sup>. Therefore, **C4** could be used as a fluorescent and colorimetric sensor for CN<sup>-</sup> detection with excellent selectivity and specificity. From the fluorescence titration, the detection limit of cyanide ion using **C4** was found to be 0.36  $\mu$ M.

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Figure 5. Chemical structures of control compounds used to understand the CN<sup>-</sup> sensing mechanism of C4.

In order to understand the binding mechanism and high selectivity of **C4** towards  $CN^{-}$ , similar kinds of photophysical studies were carried out with two control compounds DPDO and TPA (Figure 5). There is no significant change in the absorption and emission spectra of control compounds with all the anions studied including  $CN^{-}$  (Figure S17 and S18, Supporting Information). It clearly indicates that difluoroboron moiety plays a crucial role in the sensing of  $CN^{-}$ .

#### **Detection mechanism**

The detection mechanism (Scheme 2) was elucidated by both experimental (<sup>1</sup>H, <sup>11</sup>B and <sup>19</sup>F NMR titrations, HRMS spectra) and theoretical studies. In the <sup>1</sup>H-NMR of **C4**, the olefinic proton (-H<sub>a</sub>) and methyl protons (-CH<sub>3a</sub>) appeared at 6.58 ppm and 2.22 ppm respectively in the acetonitrile-d<sub>3</sub> solvent. Upon the addition of two equivalents of tetrabutylammonium cyanide, both the protons -H<sub>b</sub> and -CH<sub>3b</sub> experienced a considerable upfield shift to 5.03 and 1.55 ppm respectively. The methyl protons were merged with -CH<sub>2</sub>- protons of tetrabutylammonium cyanide (Figure 6). Besides, some changes of peak positions in the aromatic region were observed.



Scheme 2. A plausible mechanism of addition of CN  $\,$  to C4 and reversibility upon addition of excess water.



Figure 6. <sup>1</sup>H NMR spectra of compound C4 in acetonitrile-d<sub>3</sub> and after addition of 2 Equiv. CN in acetonitrile-d<sub>3</sub>.

In order to elucidate the actual interaction between the cyanide ion and **C4**, NMR titrations have been carried out with different aliquots of tetrabutylammonium cyanide from 0.1 to 2.0 equivalents by <sup>1</sup>H, <sup>11</sup>B, <sup>19</sup>F NMR spectroscopy in CDCl<sub>3</sub>. Solvent CDCl<sub>3</sub> was chosen for this experiment because the peaks due to acetonitrile and water in CD<sub>3</sub>CN appeared prominently in the aliphatic region of **C4**. Upon increasing the concentration of CN<sup>-</sup> from 0 to 2.0 equivalents a gradual decrease in intensity of the olefinic -CH and CH<sub>3</sub> protons of **C4** and increase in intensity of the new peaks at 5.03 and 1.55 ppm were noted. The olefinic proton signal at 6.4 ppm and the methyl peak at 2.3 ppm completely disappeared in the presence of excess CN<sup>-</sup> (Figure 7). The same spectral pattern was observed in <sup>19</sup>F spectra as well (Figure 8). However, <sup>11</sup>B NMR was not informative (Figure S19).



Figure 7. <sup>1</sup>H NMR spectra of titration experiment with tetrabutylammonium cyanide on C4 in CDCl<sub>3</sub>.

These results indicate that the transformation of C4 to C4-CN<sup>-</sup>, which was further confirmed by HRMS analysis. The molecular ion peak of C4 appeared at 400.1291 corresponding to C22H18BF2NO2 [M+Na]<sup>+</sup>. In the presence of 10 equivalents of CN<sup>-</sup> , C4 in acetonitrile:water (98:2) solution showed signal assignable to the formation of the C4+CN<sup>-</sup> adduct at m/z, 403.1449 (Fig. S20, Supporting Information). Based on the NMR titrations, a plausible structure for the adduct, as in Scheme 2 has been proposed. In an organic solvent, strong nucleophile CN<sup>-</sup> can attack the carbonyl carbon to give the intermediate (I) in which the olefinic and methyl protons is expected to experience upfield shifts. To our surprise, the actual NMR spectral characteristics of C4 were restored by the addition of excess water to C4-CN<sup>-</sup>. This could be due to the leaving of CN<sup>-</sup> from the C4+CN<sup>-</sup> adduct which in turn generates the starting compound (Scheme 2). The solvation of CN<sup>-</sup> in water is perhaps the reason for the above reverse reaction. The <sup>1</sup>H and <sup>19</sup>F NMR titrations reveal that there is no fluoride displacement in the presence of CN<sup>-</sup>. There are a few reports on cyanide ion sensors based on BODIPY and related compounds. The sensing mechanism proposed in the present study is different from those that are reported in these reports.[20]

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Figure 8.  $^{19}\mathsf{F}$  NMR spectra of titration experiment C4 with tetrabutylammonium cyanide in CDCl\_3.

#### **Computational Studies**

To further investigate the CN<sup>-</sup> detection mechanism using **C4**, density functional theory (DFT) calculations were performed at the B3LYP/6-31G<sup>\*</sup> level of the Gaussian 09 program to understand their electronic structures.<sup>[21]</sup> Optimization of **C4** and **C4**+CN<sup>-</sup> was performed in the gas phase. The calculated molecular orbitals and their energies are shown in Figure 9.



Figure 9. HOMO and LUMO of C4 and C4+CN<sup>-</sup>.

In **C4**, the highest occupied molecular orbital (HOMO) is localized mainly onto the triphenylamine (TPA) unit, and the lowest unoccupied molecular orbital (LUMO) is localized mostly on the dioxaborine ring and one of the phenyl ring from TPA moiety connected to it. Interestingly, the nucleophilic addition of CN<sup>-</sup> with **C4** leads to complete reversal of HOMO to LUMO and LUMO to HOMO. HOMO is localized mainly on the dioxaborine ring and LUMO is localized on the two phenyl rings perpendicular to the plane of the molecule. It confirms that the nucleophilic addition of CN<sup>-</sup> with **C4** leads to the formation of a new ICT state, which in turn responsible for the enhancement in new ICT emission peak upon increasing the CN<sup>-</sup> concentration. The increase in the energy

gap between HOMO and LUMO is accountable for the blueshifted emission in the presence of CN<sup>-</sup>.



Figure 10. Test strip detection of CN<sup>-</sup> in water.

#### Test strip detection of CN<sup>-</sup> ion

A test-strip-based assay was developed to achieve the detection of CN<sup>-</sup> in neat aqueous solution and thereby it could be used for in situ/on-site detection. We chose Whatman filter paper because this matrix ensures the probe is physisorbed well so that there is no leaching of the hydrophobic probe molecules in water. Whatman test strips were dipped into the acetonitrile solution of **C4** and left to dry in air. It was then immersed in 10  $\mu$ M aqueous solution of tetrabutylammonium cyanide. As seen in the Figure 10, significant color change from yellow to colorless was observed immediately. It proved that the test strips could be applied to detect CN<sup>-</sup> qualitatively in water for rapid detection. The test strip experiments conducted at various concentrations were not useful as the color change was not prominent at lower concentrations.

#### Conclusions

In summary, we have successfully developed a Donor-Acceptor system based on triphenylamine donor and difluoroboron  $\beta$ -diketonate acceptor. Nucleophilic addition of cyanide ion on difluoroboron  $\beta$ -diketonate completely changes the photophysical properties of **C4** and thereby offers selective detection of CN<sup>-</sup> both colorimetrically and fluorimetrically. **C4** senses the CN<sup>-</sup> with a detection limit of 0.36  $\mu$ M without any interference from other anions. Test strip detection in water and immediate response make **C4** a promising system for sensing of CN<sup>-</sup>.

#### **Experimental Section**

#### Materials and methods

Toluene and methanol were dried over sodium metal before use. Dichloromethane was freshly distilled over CaH<sub>2</sub>. <sup>1</sup>H and <sup>13</sup>C spectra were recorded on 400 MHz and 500 MHz spectrometers in CDCl<sub>3</sub> and CD<sub>3</sub>CN with tetramethylsilane (TMS) as the internal standard. IR spectra were recorded on an ATR-IR spectrometer. The progress of the reactions was monitored by TLC and visualized under UV and lodine chamber. Column chromatography was performed using silica gel 100-200 mesh, using ethyl acetate and hexane mixture as eluent. Titration studies were carried out in 10-mm quartz cell at room temperature. Tetrabutylammonium salts of the

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respective anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, HSO<sub>4</sub><sup>-</sup>, IO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>) were purchased from reputed chemical companies and used without any further purification. All spectral studies were carried out in HPLC solvents. High-resolution mass spectra (HRMS) were obtained from micro mass ESI-TOF MS and Accurate-Mass Q-TOF LC/MS system. UV-vis and fluorescent measurements were carried out on a Cary 300 Bio and Jasco FP-6300 spectrophotometer, respectively. NMR titrations were carried out using **C4** in CDCl<sub>3</sub> solution. Different equivalents (0.1 to 2) of tetrabutylammonium cyanide (from a stock of 10 mM in CDCl<sub>3</sub>) were added to a **C4** solution and the spectra were recorded.

#### Synthesis of C4

Compounds  ${\bf 2}$  and  ${\bf 3}$  were prepared by following methods from previously reported procedures.  $^{[18]}$ 

**1-(4-(Diphenyl amino) phenyl) ethan-1-one (2).** To a stirred solution of triphenylamine (2.5 g, 10.20 mmol) in dry dichloromethane (30 mL), acetyl chloride (0.8 mL, 12.23 mmol) was added dropwise for 0.5 h at 0°C. Anhydrous AlCl<sub>3</sub> (1.6 g, 12.23 mmol) was added in portionwise. Then, the reaction was brought to room temperature and stirred for 12 h. The reaction mixture was then poured into ice cooled water and neutralized with 10% aqueous Na<sub>2</sub>CO<sub>3</sub> solution and extracted with dichloromethane. The organic layers were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed using a rotavapor. The crude was purified by column chromatography using 20% EtOAc/hexanes to get the product as a pale yellow solid; Yield = 80%, R<sub>f</sub> = 0.46 in 1:5 EtOAc/hexanes; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.79 (d, *J* = 8.8 Hz, 2H), 7.31 (t, *J* = 8.4 Hz, 4H), 7.16-7.10 (m, 6H), 6.98 (d, *J* = 8.8 Hz, 2H), 2.52 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  196.6, 152.2, 146.5, 130.0, 129.7, 126.0, 124.7, 119.7, 26.4 (**Figure S1 and S2**).

**1-(4-(Diphenyl amino) phenyl) butane-1,3-dione (3).** Ethyl acetate (0.4 mL, 3.91 mmol) was added to a stirred solution of NaH (0.18 g, 4.35 mmol) and 1-(4-(diphenyl amino) phenyl) ethan-1-one **2** (0.25 g, 0.87 mmol) in dry toluene (5 mL) at room temperature under N<sub>2</sub> atmosphere. The solution was refluxed for 21 h. The reaction mixture was cooled at room temperature then neutralized with dil. HCl and extracted with EtOAc (2×20 mL). The combined organic phase was dried over anhydrous sodium sulphate. The product was purified by column chromatography using 20% of EtOAc/hexanes mixture. Yellow solid (0.23 g, yield = 80%,); R<sub>f</sub> = 0.77 in 1:5 EtOAc/hexanes; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 16.39 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.33-7.29 (m, 4H), 7.17-7.13 (m, 6H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.09 (s, 1H), 2.16 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 191.6, 183.7, 151.7, 146.6, 129.6, 128.5, 125.8, 124.5, 120.3, 95.7, 25.4; IR (neat): υ 3027, 2969, 1738, 1584, 1488, 1217, 772 cm<sup>1</sup>; HRMS (ESI): calcd for C<sub>22</sub>H<sub>19</sub>NO<sub>2</sub> [M+Na]<sup>+</sup> 352.1308, Found 352.1306 (**Figure. S3-S6**).

#### 4-(4-(Diphenylamino)phenyl)-2,2-difluoro-6-methyl-2H-1,3,2-

*dioxaborinin-1-ium-2-uide (C4).* To a stirred solution of the 1,3-diketone substrate **3** (0.06 g, 0.18 mmol) in dry dichloromethane (3 mL), BF<sub>3</sub>·OEt<sub>2</sub> (0.027 mL, 0.22 mmol) was added dropwise at room temperature and maintained for another 0.5 h. The colour of the reaction mixture changed instantly to red during the addition of BF<sub>3</sub>·OEt<sub>2</sub>. The reaction was quenched with 0.2N aqueous NaOH solution and extracted with dichloromethane solution. The crude product was further purified using column chromatography. Red solid; MP: 209-211°C; Yield = 97%, R<sub>f</sub> = 0.26 in 1:5 EtOAc/hexanes; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.87 (d, *J* = 9.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 4H), 7.24-7.18 (m, 6H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.40 (s, 1H), 2.31 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  188.2, 180.9, 154.5, 145.3, 131.3, 130.0, 126.7, 126.1, 118.3, 96.0, 24.3; <sup>11</sup>B (160 MHz, CDCl<sub>3</sub>):  $\delta$  0.91; <sup>19</sup>F (470 MHz, CDCl<sub>3</sub>):  $\delta$  -140.1; IR (neat):  $\upsilon$  3036, 1544, 1489, 1336, 754, 697, 517 cm<sup>-1</sup>; HRMS (ESI): calcd for C<sub>22</sub>H<sub>18</sub>BF<sub>2</sub>NO<sub>2</sub> [M+Na]<sup>+</sup> 400.1291, Found 400.1291 (**Figure. S7-S12**).

#### Limit of Detection:

The limit of detection (LOD) for **C4** was calculated from a fluorescence titration. To determine the S/N ratio, the fluorescence intensity of **C4** without CN<sup>-</sup> was measured ten times and the standard deviation of blank measurements was determined to be 0.0572. The fluorescence intensity plot [I/I<sub>0</sub>-1] varies almost linearly vs. the concentration of CN<sup>-</sup> in the range of 44 – 200  $\mu$ M. The limit of detection was then calculated from the following equation,

 $LOD = 3\sigma/k$ 

Where  $\sigma$  is the standard deviation of blank measurements, m is the slope obtained from the plot of  $[I/I_o\text{-}1]$  verses CN concentration. The limit of detection was obtained to be 0.36  $\mu\text{M}$  which was lower than the WHO limit of 1.9  $\mu\text{M}$  for CN  $^\circ$  in drinking water. This indicates that C4 was highly sensitive for the detection of CN anion.

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Keywords: Triphenylamine • difluoroboron  $\beta$ -diketonate • Fluorescent sensor • Colorimetric sensor • Cyanide ion • Test strip detection

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### Entry for the Table of Contents

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A triphenylamine linked difluoboron  $\beta$ -diketonate based sensor can detect cyanide ion in organic–aqueous media with high selectivity and sensitivity. The probe embedded in cellulose test strip enables naked-eye detection of CN<sup>:</sup> in a neat aqueous medium.

\*Cyanide Sensing